

Excess Enthalpies (H^E) for 2-Butoxyethanol/Water and Determination of Liquid-Liquid Equilibrium Phase Boundaries from Fits to H^E of Redlich-Kister, Pade, and Critical-Scaling Equations

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Excess enthalpies (H^E) for the binary *n*-butanol/water measured by isothermal flow calorimetry at 30 and 55°C, and nonionic amphiphile 2-butoxyethanol/water at 10 different temperatures (from 48.5 to 70°C) reported in the literature were analyzed for the determination of phase boundaries. H^E exhibited S-shape behavior in the former system and U-shape behavior in the latter system.

When the H^E data in the single-phase were fitted by semi-empirical polynomials and critical-scaling equations, plots of specific H^E vs. weight fraction provided more accurate fitting with fewer parameters than conventionally drawn molar H^E vs. mole fraction plots. This was due to the enhanced symmetry of specific H^E vs. weight fraction plots.

Liquid-liquid equilibrium phase boundaries between the single- and two-phase regions were determined from H^E . The phase boundary points were obtained as the intersections of the curve and the straight line, which describe the composition dependence of H^E for the single- and two-phase regions, respectively. When Redlich-Kister (RK) and Padé polynomials were employed, the phase boundary points could be determined for the *n*-butanol/water but not for the 2-butoxyethanol/water. These results imply that correct phase boundaries may not be obtained with the semi-empirical polynomials when H^E behavior is of the U-type. However, when the critical-scaling equations for H^E of binary mixtures were used, the phase boundaries were obtained accurately, irrespective of the type of H^E data.

Introduction

Thermodynamic excess functions such as excess free energy, excess enthalpy, and excess volume are essential to understanding nonideal behavior of mixtures. This nonideality is primarily caused by size effects and interactions of the molecules which comprise the mixture (Sandler, 1999). While excess volume measurements of the mixture may provide molecular size information, excess enthalpy yields information about the molecular interactions and the extent to which real mixtures deviate from ideality. Hence, excess enthalpy may be more important for or relevant to development of molecular models which account for nonideality.

An excess function is defined as the difference between an actual quantity and the quantity for an ideal mixture at the same conditions. Since the enthalpy change for the ideal mixing is zero, the excess enthalpy and the heat of mixing are identical (Smith *et al.*, 1996).

For this reason these two terms are used interchangeably in this article.

Excess enthalpy, H^E , is found in various uses such as in determinations of other excess quantities (Christensen *et al.*, 1988), of equilibrium phase compositions (Pando *et al.*, 1983; Rowley and Battler, 1984; Christensen *et al.*, 1988), of temperature dependence of activity coefficients, and also of critical micelle concentrations (Andersen and Birdi, 1991).

In this work, heats of mixing or excess enthalpies for the binary *n*-butanol/water at 30°C and 55°C were measured by isothermal flow calorimetry. These data along with H^E 's for the nonionic amphiphile 2-butoxyethanol/water reported in the literature (Lim *et al.*, 1994a) were analyzed for the determination of liquid-liquid phase boundaries.

For the determination of phase boundaries or phase diagrams, there have been used various methods such as visual observation, chemical analysis, phase volume method (Lim *et al.*, 1993) calorimetry (Smith *et al.*, 1989), and NMR (Ulmius *et al.*, 1977). The first three methods are conventional and used more widely than the others. These methods use the phase separation of the sample mixture. When the mixture is left stand long

enough to reach equilibrium, the number of phases are observed and if there are separated phases, samples of each phase are analyzed or the phase volumes are measured to yield phase boundaries and tie-line compositions. However, these methods pose some experimental difficulties as they are often time-consuming and may require efforts of many months. When a surfactant is a component of the system, these difficulties can be greatly compounded because the surfactant system often forms a stable dispersion. And more importantly, visual observation and phase volume method may be inapplicable or applicable with great difficulty at best to the phase boundary determination at high pressures. Phase behavior study at high pressures is essential for supercritical extractions and enhanced oil recovery. To circumvent these problems calorimetry or NMR may be used.

Excess enthalpies for the system we studied have been reported in the literature: Goodwin and Newsham (1971), Belousov and Panov (1970, 1976), Marongiu *et al.* (1984) for the *n*-butanol/water; and Onken (1959), Scatchard and Wilson (1964), Pathak *et al.* (1970), Kusano *et al.* (1973), Siu and Koga (1989) for 2-butoxyethanol/water. For the latter system, most of the reported data were measured at temperatures below T_c , i.e., in the single-phase region. At temperatures above T_c , Lim *et al.* (1994a) reported H^E 's at ten different temperatures and also several scattered data points at 60, 80, and 100°C (Onken, 1959) and at 65 and 85°C (Scatchard and Wilson, 1964) have been reported.

When LLE phase boundaries are determined from H^E , the data are fitted by semi-empirical polynomials (e.g., Redlich-Kister or Padé) or by thermodynamic models. For binary mixtures H^E vs. composition plots show curved behavior in the single-phase region and straight-line behavior in the two-phase region. At the phase boundary point the curve and the line must meet. Hence, usually the phase boundary is determined by (i) fitting the theory to the single-phase data, (ii) fitting a straight line to the two-phase data, and (iii) calculating the points of their intersections.

In previous studies the semi-empirical Redlich-Kister and Padé polynomials, or thermodynamic local-composition models were used to fit the single-phase data. It is quite common that the thermodynamic models do not yield accurate results for the LLE phase boundaries, as Rowley and Battler (1984) showed. Hence, using semi-empirical polynomials has been a usual resort for doing such work. Although the polynomials lack in rigorous theoretical basis, they yield satisfactory results. For the *n*-butanol/water system, this method was successful, as demonstrated in this article. However, for the 2-butoxyethanol/water system, the curve for the single phase and the line for the two phases had either no intersection or intersections quite different from the correct phase boundary points. Therefore, the LLE phase boundaries could not be

found. Still, the polynomials fitted quite well the single-phase data over virtually the whole range of compositions. These results point to the fact that, when LLE phase boundaries are determined from H^E , one should use a theory that describes adequately H^E in the single-phase region and at the same time yields accurate results. Lim *et al.* (1994b) derived critical-scaling equations for H^E of binary mixtures and used these equations for the determination of LLE phase compositions. Their equations yielded accurate results, and they were in excellent agreement with literature data. A brief explanation of their theory and its application to butanol/water and 2-butoxyethanol/water are presented.

Also, the partial molar excess enthalpies and the temperature dependence of activity coefficients for the 2-butoxyethanol/water system were determined from H^E , and the latter is reported in this article. They were determined by fitting the Redlich-Kister (RK) polynomial to H^E . The H^E versus molar concentration plots are highly asymmetric due to the disparity of component's molecular weights (2-butoxyethanol/water = 118/18), and the symmetry is substantially increased when H^E is plotted against weight fraction. Such symmetry is essential to having excellent fits with fewer parameters. Hence, H^E versus weight fraction was fitted by the polynomial and excellent fits could be obtained with only 4 parameters.

1. Experimental Section

Material: The amphiphile 2-butoxyethanol, $C_4H_9OC_2H_4OH$, and *n*-butanol were from Aldrich. 2-Butoxyethanol is often denoted as C_4E_1 , where C_4 and E_1 indicate the number of carbons in the hydrophobic chain and of ethoxylate groups in the hydrophilic part, respectively. Each of the amphiphiles had a stated purity of 99%, which was confirmed by gas chromatography. The chemicals were used as received, and the water was distilled and deionized.

Excess Enthalpy Measurements: Excess enthalpies were measured at atmospheric pressure with a Hart Scientific (Provo, Utah) Model 503 isothermal flow calorimeter. The main components of the calorimeter were the reaction (or mixing) vessel, isothermal shields, air bath, the isothermal control unit, feed pumps, and flow controller programmer. The reaction vessel consisted of an equilibration coil with a "mixing wire". The wire promoted thorough mixing of the fluids as they flowed through the coil. Without the mixing wire inside the equilibration coil the mixing was inadequate. Figure 1 shows the equilibration coil with the crimped mixing wire where mixing took place. The equilibration coil was constructed of 1.83 m long, 0.159 cm o.d., 0.13 mm thin, stainless steel tubing which were soldered together, so that the two inlet streams ran countercurrent to the exit stream. The mixing wire was crimped wire of 1.5 m in length (Christensen *et al.*, 1981; Christensen and Izatt, 1984).

The excess enthalpy during the mixing of the fluids was measured within ± 0.005 J by counting the number of heat pulses of a controlled heater through the isothermal control unit. The controlled heater compensated the energy liberated or absorbed by the mixing and maintained the reaction vessel temperature constant to ± 0.05 mK. We estimate the accuracy of the compositions as ± 0.1 mass% and the excess enthalpy as $\pm 2\%$. A desktop computer controlled the pumps (LC-5000 Precision Pump, ISCO Inc., Lincoln, NE) and the isothermal control unit through programmers (Hart Scientific, 1987).

2. Equations for Fits of H^E in the Single-Phase Region

At each temperature the measured enthalpies were fitted by the Redlich-Kister (RK) polynomial,

$$H^E = w_1 w_2 \sum_{i=0}^l A_i (w_1 - w_2)^i$$

$$= w_1 (1 - w_1) \sum_{i=0}^l A_i (2w_1 - 1)^i \quad (1)$$

and by the Padé approximation, or rational function which was proposed first by Malanowski (1974) and further elaborated by Marsh (1977),

$$H^E = w_1 w_2 \frac{\sum_{m=0}^l B_m (w_1 - w_2)^m}{1 + \sum_{n=0}^l C_n (w_1 - w_2)^n}$$

$$= w_1 (1 - w_1) \frac{\sum_{m=0}^l B_m (2w_1 - 1)^m}{1 + \sum_{n=0}^l C_n (2w_1 - 1)^n} \quad (2)$$

Here w_1 and w_2 are the compositions of the components 1 and 2, and A_i , B_i , and C_i are fitting parameters. From Eqs. (1) and (2) one can see that the Redlich-Kister (RK) polynomials are a special case of the Padé polynomials; Eq. (2) converges to Eq. (1) when $C_j = 0$ for $j \geq 0$.

Equation (2) often works better for more complex composition dependencies. However, when the modified Redlich-Kister polynomial is used, in which Eq. (1) is divided by $[1 - k(1 - 2w_1)]$ with k being the skewness factor, asymmetric behavior of H^E for some systems can be described quite adequately (Benson *et al.*, 1986; Kurihara *et al.*, 1998).

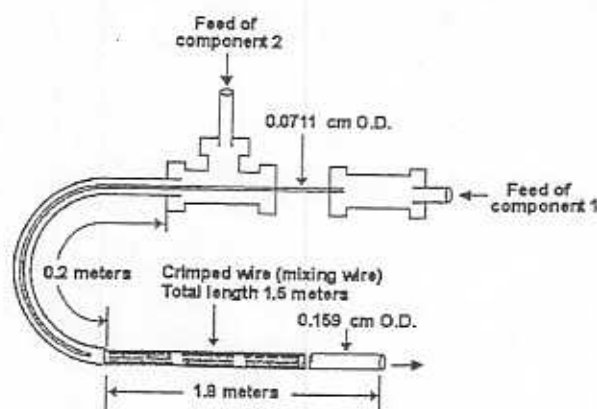


Fig. 1 Equilibrium coil including inlet connectors and mixing tube with the mixing wire

The number of terms to be used with Eqs. (1) and (2) are not known *a priori*, and it is best to use the fewest parameters possible that still represent the data accurately. Equation (2) with $m = 3$ and $n = 2$ (seven parameters) is probably the most complicated rational function of practical use.

Other equations used for H^E in the single-phase are critical-scaling equations by Lim *et al.* (1994b), who derived their equations for H^E of binary mixtures from the Widom-Kadanoff scaling treatment (Widom, 1965; Kadanoff, 1966) of free energy. Here, only the equations used for the fits are presented; details of the derivation can be found elsewhere (Lim *et al.*, 1994b). At each temperature above T_{mix} , H^E is described by

$$H^E = H_0 + \bar{A}(OP - OP_{PB})^2 + \bar{D}w + O[(OP - OP_{PB})^4] \quad (3)$$

where \bar{A} is a constant, H_0 and \bar{D} are the intercept and the slope in the two-phase region, and w is either w_1 or w_2 . The new concentration variable or order parameter, OP , is defined as

$$OP = \frac{fw}{1 + (f-1)w} \quad (4)$$

with f being a parameter and OP_{PB} being the value of OP at the phase boundary. According to the critical-scaling theory, OP varies as (Sengers, 1982)

$$OP = OP_c \pm B\varepsilon^\beta \pm C\varepsilon^{\beta+\Delta} + D\varepsilon^{1-\alpha} \quad (5)$$

where OP_c is the value of OP at T_{mix} ; B , C , and D are fitting parameters; and α , β , and Δ are universal critical-scaling exponents, the values of which are 0.11 (Fisher, 1964; Le Guillou and Zinn-Justin, 1980), 0.325

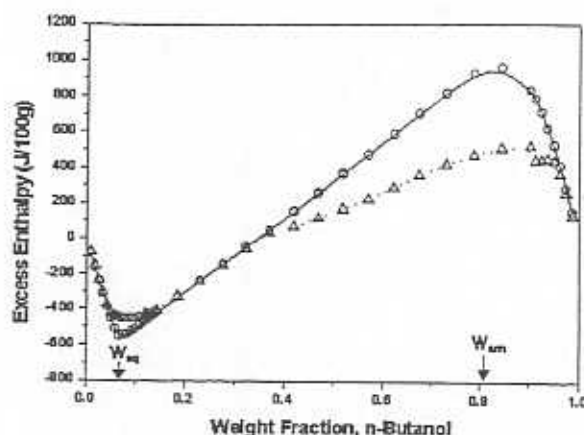


Fig. 2 Excess enthalpies measured by isothermal flow calorimetry for *n*-butanol/water at 30°C without (broken line) and with (solid line) "mixing wire"

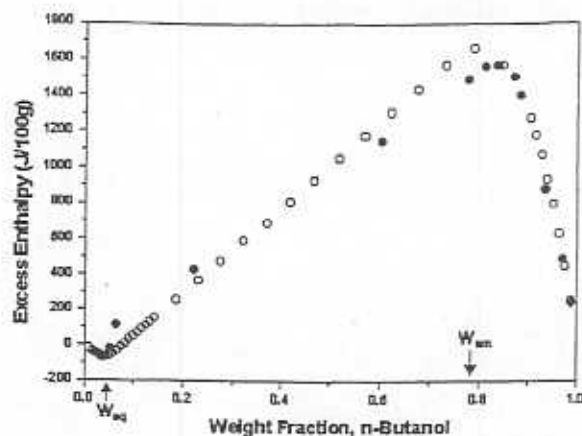


Fig. 3 Excess enthalpies for *n*-butanol/water at 55°C. Open circles, this work; Filled circles, data by Belousov and Panov (1970)

(Fisher, 1964; Le Guillou and Zinn-Justin, 1980), and 0.5 (Baker *et al.*, 1976), respectively. The sign convention in the above equation is + for $w > w_c$ (concentration at the critical point) and - for $w < w_c$. The symbol ε is the dimensionless temperature defined as

$$\varepsilon = \frac{T - T_{lc}}{T_{lc}} \quad (6)$$

If the terms higher than $(OP)^2$ are neglected in Eq. (3), then the equation can be rewritten as

$$OP - OP_{PB} = \frac{1}{\sqrt{A}} \sqrt{\frac{H^E - H_o - \bar{D}w}{1 + (f-1)w}} \quad (7)$$

Hence, if OP is plotted vs. $\sqrt{(H^E - H_o - \bar{D}w)/[1 + (f-1)]}$, OP_{PB} is obtained as the intercept; and when OP_{PB} is substituted into Eq. (4), w_{PB} (LLE phase boundary point) is obtained. If T_{lc} is known, the resulting equation has six parameters (A , B , C , D , f , and OP_c) to be found from the fit of H^E vs. concentration.

3. Results and Discussion

First, the performance of the calorimeter was tested for the *n*-butanol/water at 30 and 55°C. Figures 2 and 3 show the measured H^E data for this system. When H^E was measured without the "mixing wire" inside the reaction (or mixing) vessel (Fig. 2), the mixing of the components was inadequate. This inadequate mixing was reflected in the following observations: (i) H^E is smaller in absolute values over the whole composition range than H^E with the mixing wire and (ii) in the two-phase region which is located between w_{eq} and w_{um} , H^E is supposed to change linearly with compositions by the lever rule. However, H^E measurements

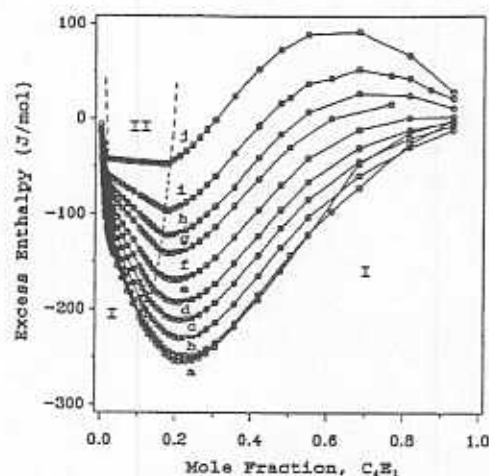


Fig. 4 Excess enthalpy in joules per mole vs. mole fraction of 2-butoxyethanol at (a) 48.472°C, (b) 48.978, (c) 50.982, (d) 52.992, (e) 54.972, (f) 57.507, (g) 60.192, (h) 62.507, (i) 64.995, and (j) 70.011. The roman numerals indicate the number of phases

without the mixing wire showed poor linearity with composition while H^E with the mixing wire gave excellent linearity. These results may serve as the criteria on whether mixing is adequate or not when H^E is measured. If mixing is more thorough in one experiment than the other, then the measured H^E of this experiment should show stronger linearity in the two-phase region and probably larger absolute values of H^E at each composition than in the other region. When H^E data measured at 55°C were compared to literature values (Fig. 3), they were in good agreement with each other. The measured and literature H^E both showed excellent linearity in the two-phase region between w_{eq} and w_{um} . However, the slope for H^E measured in this work was steeper than that of literature values and the

Table 1 Measured excess enthalpies, H^E 's, for the *n*-butanol(1)/water(2) systems

w_1	x_1	30°C		55°C	
		H^E [J/100 g]	H^E [J/mol]	H^E [J/100 g]	H^E [J/mol]
0.0081	0.0020	-83.21	-15.08	-21.55	3.91
0.0163	0.0040	-163.14	-29.76	-38.81	-7.08
0.0244	0.0061	-240.21	-44.09	-52.29	-9.60
0.0326	0.0081	-315.05	-58.20	-61.68	-11.39
0.0409	0.0103	-386.80	-71.91	-65.53	-12.18
0.0491	0.0124	-452.95	-84.75	-63.05	-11.80
0.0574	0.0146	-510.82	-96.21	-53.58	-10.09
0.0657	0.0168	-550.10	-104.30	-36.69	-6.96
0.0741	0.0191	-548.06	-104.61	-14.43	-2.76
0.0825	0.0214	-539.17	-103.61	3.18	0.61
0.0910	0.0237	-526.19	-101.81	25.98	5.03
0.0994	0.0261	-510.56	-99.47	44.29	8.63
0.1079	0.0286	-493.20	-96.76	66.16	12.98
0.1165	0.0310	-476.11	-94.07	88.21	17.43
0.1250	0.0336	-458.21	-91.18	106.57	21.21
0.1336	0.0361	-438.86	-87.96	127.26	25.51
0.1423	0.0387	-421.89	-85.18	147.31	29.74
0.1859	0.0526	-332.74	-69.76	253.36	53.12
0.2305	0.0679	-238.57	-52.06	363.02	79.22
0.2759	0.0848	-141.65	-32.26	473.27	107.77
0.3223	0.1036	-43.17	-10.29	588.27	140.18
0.3696	0.1247	49.71	12.43	691.21	172.90
0.4180	0.1486	152.88	40.29	807.92	212.91
0.4673	0.1757	259.34	72.29	929.50	259.10
0.5177	0.2069	366.98	108.72	1054.6	312.42
0.5692	0.2431	474.97	150.34	1177.6	372.76
0.6218	0.2855	586.54	199.62	1305.4	444.28
0.6756	0.3360	699.71	257.97	1436.0	529.45
0.7305	0.3972	814.53	328.25	1568.7	632.20
0.7867	0.4727	922.28	410.77	1662.4	740.41
0.8442	0.5684	957.47	477.85	1565.4	781.24
0.9030	0.6936	827.05	470.82	1270.3	723.16
0.9150	0.7234	780.10	457.14	1178.5	690.62
0.9269	0.7551	709.65	428.49	1070.3	646.24
0.9390	0.7890	621.32	386.97	930.39	579.47
0.9511	0.8253	527.29	339.14	792.61	509.79
0.9632	0.8642	414.17	275.43	626.27	416.48
0.9754	0.9060	286.61	197.33	441.21	303.77
0.9877	0.9512	152.72	109.01	249.16	177.85

measured H^E at the amphiphilic phase composition was larger. These results may indicate that our measurements were done with better mixing, judging from the results of Fig. 3. The measured H^E 's at 30 and 55°C are listed in Table 1.

Excess enthalpies for the 2-butoxyethanol/water system at ten different temperatures from 48.5 to 70°C were reported (Lim *et al.*, 1994a) and reproduced in Figs. 4 and 5. The plots are in two different units: J/mol vs. mole fraction of the amphiphile (Fig. 4), and J/100 g of the mixture vs. weight fraction of the amphiphile (Fig. 5). More details with the tabulated data and figures can be found elsewhere (Lim *et al.*, 1994a).

H^E was negative and large over the whole concentration range at lower temperatures. These large negative values indicate that there are considerable interactions between water and 2-butoxyethanol. As temperature increased, H^E also increased and became positive at high amphiphile contents. This behavior of H^E is similar to that of alcohol/water, glycol/water, and glycerol/water.

In Figs. 4 and 5, the region marked by II is the two-phase region, which is bordered on each side by the single-phase regions marked by I. In the two-phase region H^E depended linearly on the component concentration, according to the lever rule. This linearity can be seen in Fig. 4 and more clearly in Fig. 5. On the

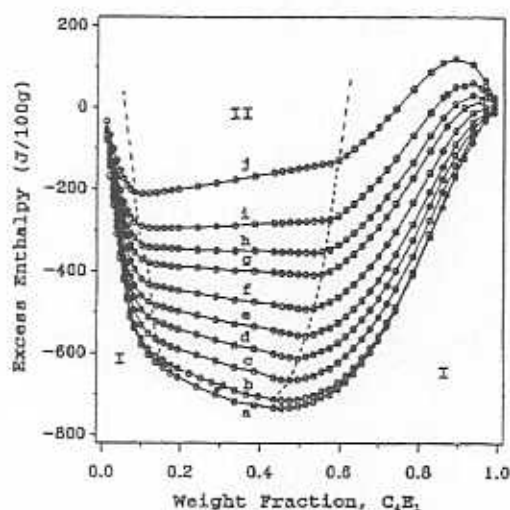


Fig. 5 Excess enthalpy in joules per 100 gram of the mixture vs. weight fraction of 2-butoxyethanol at (a) 48.472°C, (b) 48.978, (c) 50.982, (d) 52.992, (e) 54.972, (f) 57.507, (g) 60.192, (h) 62.507, (i) 64.995, and (j) 70.011. The roman numerals indicate the number of phases

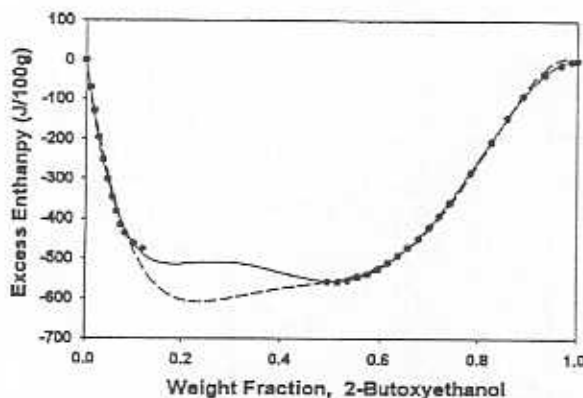


Fig. 6 Specific H^E vs. weight fraction 2-butoxyethanol/water, measured at 55°C (filled circle) and the Redlich-Kister fitting equations, Eq. (1), of 5th (broken line) and 7th (solid line) orders

aqueous side, where the phase contains mainly water (w small), the curved behavior of the single-phase region was also seen more clearly in Fig. 5. The data denoted by a and b were measured at about and slightly above the lower consolute solution temperature $T_{lc} = 48^\circ\text{C}$. Therefore, at these temperatures the linear dependence of H^E on the concentration in the two-phase region is hardly seen.

The unit of excess enthalpies in this work is in Joule per gram [J/g], because this makes the plots far more symmetric. This greater symmetry allowed accurate fitting results. For the fits of molar H^E to the Redlich-Kister polynomial, the results are significantly

Table 2 Compositions at the phase boundary points between single and 2-phase regions for the *n*-butanol/water system

T [°C]	Barton (1984)		This work	
	w_{aq}	w_{am}	w_{aq}	w_{am}
30	0.068	0.813	0.090	0.814
55	0.055	0.771	0.068	0.763

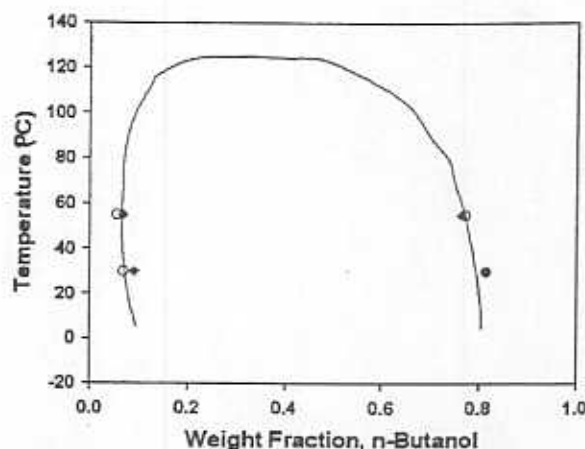


Fig. 7 A part of phase diagram of *n*-butanol/water and the phase boundary points determined with 5th-order Redlich-Kister polynomial (open circles) and critical scaling equations of Lim *et al.* (filled diamonds). The binodal represented by the curve is from Barton (1984)

improved, as the degree of the polynomial increases from the 5th to the 9th; the correlation coefficients are from 0.9606 for the 5th, 0.9935 for the 7th, and 0.9987 for the 9th, respectively. Even with the 9th-order polynomial, interpolation between the data points is undesirable because the fitting polynomial exhibits a wavy nature. Also, this polynomial has 7 parameters to be determined and this number of parameters may be the upper limit in a practical sense.

Figure 6 shows the fitting results for the specific excess enthalpy with the 4-parameter 5th-order and the 6-parameter 7th-order polynomials. The figure shows that the fit by the polynomials was excellent over the whole concentration range. The 7th-order polynomial almost exactly traced the data, and the 5th-order polynomial almost did except at very high amphiphilic contents. Even the 5th-order Redlich-Kister (RK) polynomial with 4 parameters yielded a better fit (correlation coefficient = 0.9990) than the 9th-order polynomial for the molar H^E . These results indicate that fitting results became significantly better when the symmetry of the plots was enhanced.

The LLE phase boundary points were determined usually from the intersections of the curved behavior

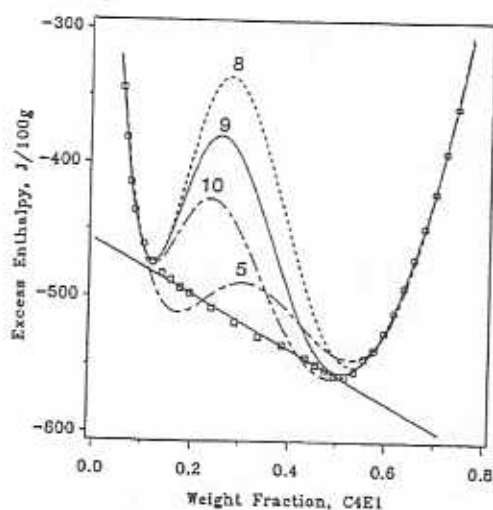


Fig. 8 Determination of LLE phase boundaries with Redlich-Kister polynomials. The numerals stand for the orders of the polynomials

of H^E in the single-phase region and the linear behavior of H^E in the two-phase region. The linear change of H^E with the amphiphile weight fraction, w , is

$$H^E = H_o + \bar{D}w \quad (8)$$

Equation (8) requires suitable equations for the single-phase region.

When the RK polynomials were used for H^E in the single-phase region of the *n*-butanol/water system (Figs. 2 and 3), the polynomials fit the data well and with the linear equation for the two-phase region they yielded two intersections that were correct LLE phase boundary points. The results are in excellent agreement with literature values (Barton, 1984), as shown in Fig. 7 and listed in Table 2. These results apparently indicate that any difficulty is hardly anticipated in determining phase boundaries for the *n*-butanol/water with this method.

However, when the same method was applied to the 2-butoxyethanol/water system, the LLE phase boundaries could not be determined. Although the RK polynomials represented the H^E data well in virtually all of the single phase region (Fig. 6), as illustrated by Fig. 8 they and the linear equation for the two-phase region yielded either no intersections or intersections quite different from the true phase boundary points. For the 5th-degree polynomial, there were two intersections. One of them could be considered as the aqueous phase boundary point, w_{aq} , but the other was far different from the amphiphilic phase boundary point, w_{am} . The other side of the W-shaped fit approached the two-phase straight line near the composition of the amphiphilic phase, but failed to meet it. For the 8th and the 9th-degree polynomials, there was no inter-

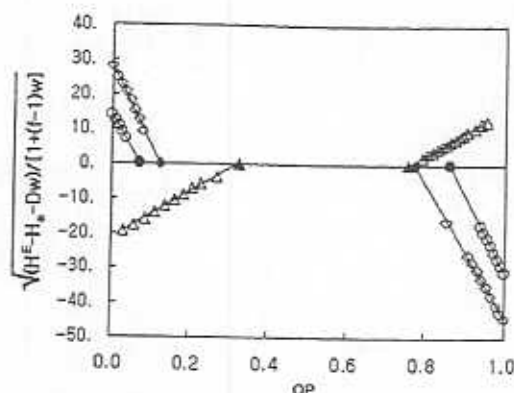


Fig. 9 OP vs. $\sqrt{(H^E - H_o - Dw) / [1 + (f-1)w]}$ of Eq. (7) for *n*-butanol/water at 30°C (○) and 55°C (◇), and for 2-butoxyethanol/water at 55°C (△). The phase boundary points are the intercepts of the x-axis

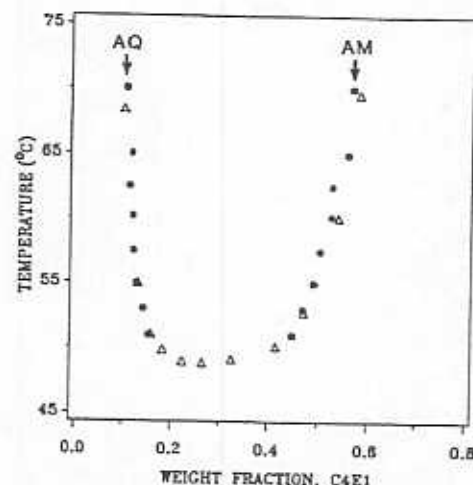


Fig. 10 LLE phase boundary points for 2-butoxyethanol/water. Triangles, Ellis (1967); filled circles, by Eq. (7)

section by any part of the Redlich-Kister fit. For the 10th-degree polynomial there were two intersections, one near the correct amphiphilic phase composition, w_{am} , but no intersection close to the composition of the aqueous phase, w_{aq} .

Similar fits were done with the Padé polynomials, Eq. (2). The Padé polynomials fit the data well in the single-phase region. However, this Padé fit also did not yield the correct intersections or phase boundary points. Only w_{aq} could be obtained by these polynomials. Note that the semi-empirical polynomials still fit the single-phase data excellently at virtually all compositions.

Because of the inability of the semi-empirical polynomials to give unique and accurate LLE phase boundary points, the critical-scaling equation by Lim *et al.* (1994b) was used. Figure 9 shows the results of

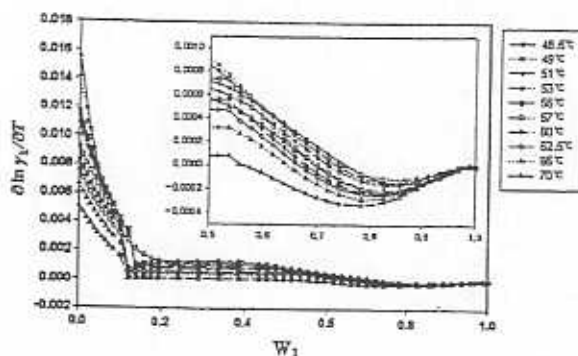


Fig. 11 Derivative of activity coefficient with respect to temperature, $\partial \ln \gamma_1 / \partial T$, of 2-butoxyethanol

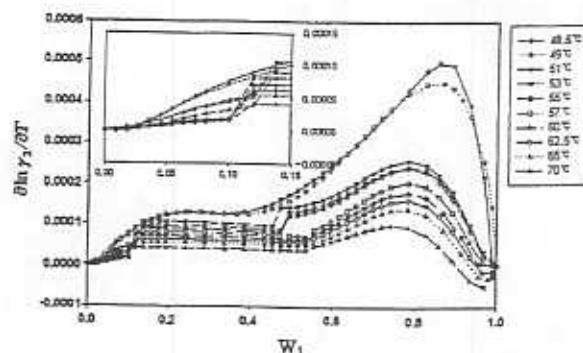


Fig. 12 Derivative of activity coefficient with respect to temperature, $\partial \ln \gamma_2 / \partial T$, of water

the fit of Eq. (7) to the H^E data of Figs. 2, 3, and 5. The equation fits the data well in the single-phase region. In this plot the slopes were the same on both the aqueous and amphiphilic sides, as the theory demands, and the LLE phase boundary points are represented by the x-axis intercepts. Three intercepts on the left are order-parameter (OP) values at the aqueous side phase boundaries, OP_{aq} 's, and three on the right are OP values at the amphiphilic side phase boundaries, OP_{am} 's. Thus-determined OP_{aq} and OP_{am} were converted to weight fractions at the aqueous and amphiphilic phase boundaries, w_{aq} and w_{am} , by Eq. (4). The results are marked in Fig. 7 for the butanol/water and Fig. 10 for the 2-butoxyethanol/water. These figures show that the results are in excellent agreement with literature.

When phase boundary points are determined from excess enthalpies and semi-empirical polynomials that depict H^E behavior in the single phase region, it seems that one may face some serious problems with this method. When the overall H^E behavior is of S-type like H^E of the butanol/water system, there may be little difficulty obtaining phase boundary points with the polynomials. However, when H^E behavior is of U-type like H^E of the 2-butoxyethanol/water system, this method may not yield correct phase boundary points. In this case the polynomials and the linear equation in the two-phase region may have no intersection at all, may have one intersection only, or may have two intersections but with one intersection representing the phase boundary point incorrectly. In contrast to the semi-empirical polynomials, critical-scaling equations of H^E provided correct phase boundary points, whether H^E behavior is S-type or U-type.

From the fits of the RK polynomials to H^E , partial molar excess enthalpies of 2-butoxyethanol and water in their mixtures were calculated using the 5th-order RK polynomial. The RK polynomials fit of the H^E data is exemplified in Fig. 6. Since the activity coefficient γ is related to the partial molar excess enthalpy, \bar{H}^E_i , through the equation

$$\left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P,x} = - \frac{\bar{H}^E_i}{RT^2} \quad (9)$$

the temperature derivative of the component activity coefficient, $\partial \ln \gamma / \partial T$, were also calculated and the results are shown in Figs. 11 and 12. The quantity $\partial \ln \gamma / \partial T$ displayed a curved behavior in the single-phase region but it was constant in the two-phase region. At the phase boundaries $\partial \ln \gamma / \partial T$ experienced an abrupt change. However, at temperatures (48.5 and 49°C) just above T_c , $\partial \ln \gamma / \partial T$ exhibits no sharp discontinuity. As the amphiphile mole fraction x_1 increased, the quantity $\partial \ln \gamma_1 / \partial T$ for 2-butoxyethanol decreased and $\partial \ln \gamma_2 / \partial T$ for water increases, reached a maximum around $x_1 = 0.8$ and then decreased. Overall, $\partial \ln \gamma / \partial T$ for 2-butoxyethanol was larger than that for water and substantially larger at low x_1 in particular.

The values of $\partial \ln \gamma / \partial T$ were compared with those determined from VLE data. Scatchard and Wilson (1964) reported VLE data at 5 temperatures (5, 25, 45, 65, 85°C) and eight concentrations in the amphiphile-rich region ($w_1 = 0.64$ –0.99). Hence, the comparison was made only at 65°C because this temperature is common for the VLE reported and LLE of this work. The $\partial \ln \gamma / \partial T$ calculated from VLE was slightly larger than that from LLE. For example, the values were 1.6×10^{-4} vs. $1.0 \times 10^{-4} \text{ K}^{-1}$ at $w_1 = 0.64$, and -2.7×10^{-5} vs. $-2.0 \times 10^{-5} \text{ K}^{-1}$ at $w_1 = 0.93$ (Lim, 2000).

Conclusion

For the determination of LLE phase boundaries from excess enthalpies, semi-empirical polynomials (Redlich-Kister and Padé) and theory-based critical-scaling equations for the excess enthalpy of binary systems were tested. When there was a substantial disparity between molecular weights of the components, the plots of specific enthalpy vs. component weight fraction were more symmetric than conventionally drawn plots of molar enthalpy vs. mole fraction. This

enhanced symmetry yielded much more accurate fitting of semi-empirical polynomials to the data.

Although the polynomials and the critical-scaling equations fit the enthalpy data equally well in the single-phase regions, the polynomials could not always yield correct phase boundaries. For the S-shape H^E data of *n*-butanol/water, the polynomials gave the correct LLE phase boundaries. However, for the U-shape H^E data of 2-butoxyethanol/water, they did not. These results imply that correct phase boundaries may not be obtained with the semi-empirical polynomials when H^E behavior is of U-type. In contrast, the LLE phase boundaries could be determined correctly with the critical-scaling equations, irrespective of the type of H^E data.

The temperature dependence of the component activity coefficient, $\partial \ln \gamma_i / \partial T$, was determined from the fits of RK polynomials to H^E . The quantity $\partial \ln \gamma_i / \partial T$ displayed a curved behavior in the single-phase region, invariance in the two-phase region, and a sharp discontinuity at the phase boundaries. Over the whole concentration range, $\partial \ln \gamma_i / \partial T$ was larger for 2-butoxyethanol than that for water.

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Nomenclature

A_i	= coefficient in the Redlich-Kister polynomial, Eq. (1)
\bar{A}	= coefficient in Eq. (3)
B_n	= coefficient in the numerator of the Padé polynomial, Eq. (2)
C_n	= coefficient in the denominator of the Padé polynomial, Eq. (2)
$C_i E_i$	= 2-butoxyethanol
\bar{D}	= coefficient in Eq. (3)
f	= fitting parameter in Eq. (4)
H^E	= excess enthalpy or heat of mixing
H_0	= the intercept of the y-axis, Eq. (3)
\bar{H}^E	= molar excess enthalpy [J/mol]
\bar{H}_i^E	= partial molar excess enthalpy of component i [J/mol]
$h(w)$	= fitting equation of excess enthalpy [J/g]
k	= skewness factor
M_1, M_2	= molecular weights of component 1 and 2 [g/mol]
N	= total mole numbers
N_i	= moles of component i
OP	= order parameter
OP_c	= OP values at the critical point
OP_{PB}	= OP values at the phase boundary
R	= universal gas constant [Pa m ³ /(mol K)]
RK	= Redlich-Kister
T	= temperature [°C]
T_{lc}	= lower critical endpoint temperature [°C]
w	= weight fraction
w_{am}	= composition of amphiphile at the amphiphilic phase boundary, in weight fraction
w_{aq}	= composition of amphiphile at the aqueous phase boundary, in weight fraction

w_i	= weight fraction of the amphiphile 2-butoxyethanol
x_i	= mole fraction of the amphiphile 2-butoxyethanol
α	= universal critical scaling exponent of which value is 0.11
β	= universal critical scaling exponent of which value is 0.325
ε	= dimensionless temperature, defined in Eq. (6)
γ_i	= activity coefficient of component i
Δ	= universal critical scaling exponent of which value is 0.50

Literature Cited

- Andersen, S. I. and K. S. Birdi; "Aggregation of Asphaltenes as Determined by Calorimetry," *J. Colloid Interface Sci.*, **142**, 497-502 (1991)
- Baker, G. A., Jr., B. G. Nickel, M. S. Green and D. I. Meiron; "Ising-Model Critical Indices in Three Dimensions from the Callan-Symanzik Equation," *Phys. Rev. Lett.*, **36**, 1351-1354 (1976)
- Barton, A. F. M., ed.; *Alcohols with Water, Solubility Data Series*, Pergamon, Oxford, England (1984)
- Belousov, V. P. and M. Y. Panov; "ТЕПЛОТЫ СМЕШЕНИЯ ЖИДКОСТЕЙ. VI" *Vestn. Leningrad Univ. Fiz. Khim.*, **10**, 111-115 (1970)
- Belousov, V. P. and M. Y. Panov; "ТЕПЛОТЫ СМЕШЕНИЯ ЖИДКОСТЕЙ. XI" *Vestn. Leningrad Univ. Fiz. Khim.*, **2**, 149-150 (1976)
- Benson, G. C., M. K. Kumaran, C. J. Halpin and P. J. D'Arcy; "Thermodynamic Properties for (3,3-Dimethylbutan-1-ol + *n*-Hexene) at 298.15 K," *J. Chem. Thermodyn.*, **18**, 1007-1014 (1986)
- Christensen, J. J. and R. M. Izatt; "An Isothermal Flow Calorimeter Designed for High Temperature, High Pressure Operation," *Thermochim. Acta*, **73**, 117-129 (1984)
- Christensen, J. J., L. D. Hansen, R. M. Izatt, D. J. Eatough and R. M. Hart; "Isothermal, Isobaric, Elevated Temperature, High Pressure Flow Calorimeter," *Rev. Sci. Instrum.*, **52**, 12261-12231 (1981)
- Christensen, J. J., R. L. Rowley and R. M. Izatt, eds.; *Handbook of Heat of Mixing, Supplementary Volume*, John Wiley, New York, USA (1988)
- Ellis, C. M.; "The 2-Butoxyethanol-Water System," *J. Chem. Educ.*, **44**, 405-407 (1967)
- Fisher, M. E.; "Correlation Functions and the Critical Region of Simple Fluids," *J. Math. Phys.*, **5**, 944-962 (1964)
- Goodwin, S. R. and D. M. T. Newsham; "A Flow Calorimeter for the Determination of Enthalpies of Mixing of Liquids: Enthalpies of Mixing of Water + *n*-Propanol and Water + *n*-Butanol at 30°C," *J. Chem. Thermodyn.*, **3**, 325-334 (1971)
- Hart Scientific; *Instruction Manual Model 501 Flow Calorimeter*, Provo, Utah, USA (1987)
- Kadanoff, L. P.; "Scaling Laws for Ising Models near T_c ," *Physics*, **2**, 263-272 (1966)
- Kurihara, K., T. Iguchi, K. Ochi and K. Kojima; "Measurement and Correlation of Excess Molar Enthalpies for the 2-Butanol + Water and Methanol + Cyclohexane Systems with Limited Miscibility at 283.15, 288.15, and 298.15 K," *Fluid Phase Equilib.*, **144**, 169-180 (1998)
- Kusano, K., J. Suurkuusk and I. Wadso; "Thermochemistry of Solutions of Biochemical Model Compounds. 2. Alkoxyethanols and 1,2-Dialkoxyethanes in Water," *J. Chem. Thermodyn.*, **5**, 757-767 (1973)
- Le Guillou, J. C. and J. Zinn-Justin; "Critical Exponents from Field Theory," *Phys. Rev. B*, **21**, 3976-3998 (1980)
- Lim, K.-H.; "Excess Enthalpies and Activity Coefficients for the Binary Nonionic Amphiphile 2-Butoxyethanol/Water System," *J. Korean Oil Chem. Soc.*, **17**, 141-147 (2000)
- Lim, K.-H., J. S. Reckley and D. H. Smith; "Liquid-Liquid Phase Equilibrium in Binary Mixtures of the Nonionic Amphiphile 2-

- (2-Hexyloxyethoxy)ethanol and Water," *J. Colloid Interface Sci.*, **161**, 465-470 (1993)
- Lim, K.-H., W. B. Whiting and D. H. Smith; "Excess Enthalpies and Liquid-Liquid Equilibrium Phase Compositions of the Nonionic Amphiphile 2-Butoxyethanol and Water," *J. Chem. Eng. Data*, **39**, 399-403 (1994a)
- Lim, K.-H., M. Ferer and D. H. Smith; "Critical-Scaling Theory of Binary Excess Enthalpies and Its Use to Determine Liquid-Liquid Equilibrium Phase Compositions," *J. Chem. Phys.*, **100**, 8284-8292 (1994b)
- Marongiu, B., I. Ferino, R. Monaci, V. Solinas and S. Torrazza; "Thermodynamic Properties of Aqueous Non-Electrolyte Mixtures. Alkanols + Water Systems," *J. Mol. Liquids*, **28**, 229-247 (1984)
- Onken, U. Z.; "Die Thermodynamischen Funktionen des Systems Wasser/Butylglykol," *Elektrochem.*, **63**, 321-327 (1959)
- Pando, C., J. A. R. Renuncio, R. S. Schofield, R. M. Izatt and J. J. Christensen; "The Excess Enthalpies of Carbon Dioxide + Toluene at 308.15, 385.15, and 413.15 K from 7.60 to 12.67 MPa," *J. Chem. Thermodyn.*, **15**, 747-755 (1983)
- Pathak, G., S. S. Katti and S. B. Kulkarni; "Calorimetric Studies on the Heats of Mixing of Cellosolve-Water Systems," *Indian J. Chem.*, **8**, 357-361 (1970)
- Rowley, R. L. and J. R. Battler; "Local-Composition Models and Prediction of Binary Liquid-Liquid Binodal Curves from Heat of Mixing," *Fluid Phase Equilib.*, **18**, 111-130 (1984)
- Sandler, S. I.; *Chemical and Engineering Thermodynamics*, 3rd ed., Wiley, New York, USA (1999)
- Scatchard, G. and G. M. Wilson; "Vapor-Liquid Equilibrium. XIII. The System Water-Butyl Glycol from 5 to 85°C," *J. Am. Chem. Soc.*, **86**, 133-137 (1964)
- Sengers, J. V.; "Universality of Critical Phenomena in Classical Fluids," *Phase Transitions-Cargese 1980*, M. Levy, J.-C. Le Guillou and J. Zinn-Justin, eds., p. 95-135, Plenum, New York, USA (1982)
- Siu, W. and Y. Koga; "Excess Partial Molar Enthalpies of 2-Butoxyethanol and Water in 2-Butoxyethanol-Water Mixtures," *Can. J. Chem.*, **67**, 671-676 (1989)
- Smith, D. H., G. L. Covatch and R. O. Dunn; "Calorimetric Phase Studies of Model Amphiphilic Petroleum Recovery Systems," *ACS Symp. Series*, **396**, 290-304 (1989)
- Smith, J. M., H. C. Van Ness and M. M. Abbott; *Introduction to Chemical Engineering Thermodynamics*, 5th ed., McGraw-Hill, New York, USA (1996)
- Ulmus, J., H. Wennerstrom, B. Lindblom and G. Arvidson; "Deuteron Nuclear Magnetic Resonance Studies of Phase Equilibria in a Lecithin-Water Systems," *Biochem.*, **16**, 5742-5748 (1977)
- Widom, B.; "Equation of State in the Neighborhood of the Critical Point," *J. Chem. Phys.*, **43**, 3898-3905 (1965)